Energy, Mines and Resources Canada | Énergie, Mines et Ressources Canada

CANMET

Canada Centre for Mineral and Energy Technology | Centre canadien de la technologie des minéraux et de l'énergie

REVERSE OSMOSIS FRACTIONATION OF PETROLEUM AND SYNTHETIC CRUDE DISTILLATES

B.A. Farnand and H. Sawatzky
Hydrocarbon Processing Research Laboratory

Patent Submission

This document is an unedited interim report prepared primarily for discussion and internal reporting purposes. It does not represent a final expression of the opinion of the Canada Centre for Mineral and Energy Technology (CANMET)

Ce document est un rapport provisoire non-révisé et rédigé principalement pour fin de discussion et de documentation interne. Il ne représente nullement l'expression définitive de l'opinion du Centre canadien de la technologie des minéraux et de l'énergie (CANMET)

ENERGY RESEARCH PROGRAM
ENERGY RESEARCH LABORATORIES
ERP/ERL 84-54(TR)

MICROMEDIA

Reverse Osmosis Fractionation of Petroleum and Synthetic Crude Distillates

by

Brian A. Farnand* and Henry Sawatzky*

ABSTRACT

The utility of porous reverse osmosis fractionation that might have application for the upgrading of petroleum and synthetic crude distillates or for the separation of components for chemical feedstocks is claimed.

As an example, the reverse osmosis separation of aromatic from non-aromatic components in naphtha and middle distillate fractions using cellulose acetate and cellulose acetate butyrate is described.

---

* Research Scientist, Hydrocarbon Processing Research Laboratories, Energy Research Laboratories, CANMET, Energy, Mines and Resources Canada, Ottawa. K1A 0G1

Le Fractionationnment des Distillats de Pétroles Naturels et de Pétroles Synthetiques Par L'Osmose Inverse

par

Brian A. Farnand* et Henry Sawatzky*

RESUME

Nous avons décrit l'usage des membranes poreuses d'osmose inverse dans un procedé visant l'ammélioration des distillats de pétroles naturels et de pétroles synthetiques. L'usage des membranes faites d'acétate de cellulose et de co-acétate-butyrate de cellulose pour changer la concentration des aromatiques dans les naphthas et les gas-oils legeres sont presentées comme des examples du procedé.

---

* Chercheur scientifique, Laboratoire de recherche sur le traitement des hydrocarbures, Laboratoires de recherche sur l'énergie, CANMET, Energie, Mines et Ressources Canada, Ottawa K1A 0G1

Background of the Invention

1. Field of the Invention

This invention is concerned with the application of reverse osmosis separation processes for the fractionation of hydrocarbon distillate in petroleum and synthetic crude refining and upgrading process for both fuel, petrochemical, and other non-fuel uses.

2. Background

Distillation is the most common process for the fractionation of petroleum into various products such as transportation fuels, lubricants, petrochemical feedstocks, and for other non-fuel uses. This method of fractionation has been successful with conventional light petroleum and the product streams have required little further refining. However, as the quality of available crude petroleum decreases and as synthetic crudes become more prevalent, the product streams require severe upgrading to maintain current quality standards. Another problem facing refiners is lead phasedown for gasoline, where the present fuel quality specifications must be met by performing more intensive reforming of low quality fuels. These upgrading measures are applied to the entire stream and losses of high quality components occur as well as high consumption of hydrogen due to production of undesired gas. The selective removal of either high- or low-quality components has been considered by using complex separations such as liquid extraction and adsorption/desorption processes. The current strategy for handling low quality fuels is upgrading of the entire product and acceptance of the loss of energy and product, as well as the supplementary hydrogen consumed.

Summary of the Invention

The invention is a method for the selective concentration of the aromatic and non-aromatic components of petroleum and synthetic crude distillate by reverse osmosis membranes. The separation is based upon the different surface affinities of the different components of the petroleum and synthetic crude distillate with respect to the membrane surface, and their permeation through the membrane under pressure.

Description of the Process

This invention is the application of reverse osmosis membranes to selectively fractionate petroleum and related distillates. In distillation, the basis for fractionation is the relation of vapour pressures of various components. This does not enable the selective removal of different component types, since the fractionation is not based upon the chemical nature of the components. In reverse osmosis, the relative affinity of various components for the membrane surface in addition to their size and shape is the basis of the fractionation. This affinity is determined by the interaction of the chemical properties of the components and the functional qroups presented by the surface of the membrane. Since petroleum and synthetic crude distillates consist of certain given types of components which are desirable without additional processing for product quality, a membrane of suitable surface composition can be chosen and the desired components can be either selectively removed as reverse osmosis permeate or concentrated as reverse osmosis retentate. Both cases involve two product streams: one enriched in the desired components; and the other depleted in the desired components. According to the contribution to the quality of the product, one of these two streams can be severely upgraded without the degradation of the desirable components which have been concentrated in the other stream. The invention is also relevant to the separation of petroleum and synthetic crude components for use as chemical feedstocks or other purposes.

A schematic of this fractionation is shown in Fig. 1. The examples that are given in the following description involve static cells. More impressive results would be expected for systems in which the feeds were circulated or if the ratio of membrane areas to volume of feeds were increased.

Examples

1. Cellulose acetate butyrate (CAB) membranes were fabricated as for use in aqueous reverse osmosis. These were subjected to solvent exchange from water to isopropanol by immersion in several steps involving successively more concentrated isopropanol in water solutions for one half hour in each step until pure isopropanol was used. Then the membranes were

subjected to solvent exchange in the same manner with heptane. The membranes were then inserted into a static reverse osmosis cell as shown in Fig. 2. The naphtha (IBP to 200°C boiling range) sample was placed on the high pressure side of the membrane and nitrogen gas pressure was used to cause permeation. After adequate volume for displacement of the heptane from the membrane had permeated the receiver was changed. Samples of permeate were collected and analyzed for the benzene, toluene, and xylenes (BTX) content, as shown in Table 1. The liquid remaining on the high pressure side of the membrane was recovered and also analyzed. Comparison of BTX concentration in the permeate and the retentate are shown in Table 1. It is apparent that the BTX content is enriched in the permeate when compared to the high pressure side.

2. Cellulose acetate (CA) membranes were fabricated as for aqueous reverse osmosis and subjected to solvent exchange with isopropanol and then with heptane. These membranes were inserted into a static reverse osmosis apparatus as shown in Fig. 2 and naphtha was placed on the high pressure side of the membrane. Under nitrogen gas pressure, the permeate was collected and analyzed for BTX content and is compared in Table 2 to the BTX content of the liquid remaining on the high pressure side of the membrane. These results do not show the same degree of enrichment as for the CAB membrane case.

3. A cellulose acetate membrane was subjected to solvent exchange with isopropanol and then to light gas oil. The membrane was loaded into a static reverse osmosis cell and middle distillate (boiling range of 200°C to 350°C) was placed on the high pressure side. AT 10 000 kPa operating pressure and room temperature, samples of the permeate and the original feed were collected and analyzed for paraffin, olefin, naphthene, and aromatic content by combined gas chromatography, mass spectrometry, and nuclear magnetic resonance, as shown in Table 3. The permeate was enriched in aromatics and naphthenes and depleted in paraffins when compared to the light gas oil.

4. A cellulose acetate butyrate membrane was fabricated as in example 1 and subjected to solvent exchange as in example 3. The membrane was inserted into a static reverse osmosis cell and a sample of light gas oil was

placed on the high pressure side. The permeate and the liquid remaining on the high pressure side were collected at an operating pressure of 5,000 kPa and room temperature. The experiment was repeated with a fresh sample of light gas oil. The analyses of Table 4 were obtained from these experiments. The permeate was enriched in aromatics and depleted in paraffins and naphthenes and the liquid remaining on the high pressure side of the membrane was conversely affected.

Claims

1. A process for the fractionation of petroleum and synthetic crude distillates into components of different chemical nature by using reverse osmosis membranes.

2. A process as in claim 1 where the selectivity of the separation can be modified by changing the membrane material and the pore size of the membrane.

3. A process for the fractionation of petroleum and synthetic crude distillate on a continuous basis. A possible configuration is presented in Figure 3.

4. A process as in claim 3 where multiple stages are used to obtain a magnified separation effect when compared to a single membrane separation.

5. A process as in claim 1 for the selective removal of groups of components based upon their affinity to the membrane surface, with their removal by concentration on the high pressure side of the membrane or by their selective permeation through the membrane.

6. A process based upon the previous claims which use membranes in a multi-stage type of separation with membranes of identical materials or with membranes of different materials, or with different operating pressures.

TABLE 1 Results of Example 1, Cellulose Acetate Butyrate Membrane and Naphtha

BTX, weight %[a]			Pressure
High Pressure Side (Retentate)	Permeate	Ratio[b]	kPa
3.15	3.30	1.07	5,000
3.16	3.53	1.12	5,000
2.97	3.40	1.14	8,000
3.01	3.50	1.16	8,000
6.97	8.99	1.29	8,000
36.84	47.13	1.28	8,000

[a] Weight % $\pm$ 0.02.

[b] Ratios in excess of 1.2 are considered to be viable multistage fractionation processes.

TABLE 2 Results of Example 2, Cellulose Acetate Membrane and Naphtha

BTX, weight %[a]			Pressure
High Pressure Side	Permeate	Ratio	kPa
3.05	3.20	1.05	8,000
3.24	3.39	1.05	6,000
3.08	3.26	1.06	4,000

[a] Weight % $\pm$ 0.02

Table 3 Results of Example 3, Cellulose Acetate Membrane and Middle Distillate.

Weight %

	Paraffins	Olefins	Naphthenes	Aromatics
Permeate	17.9	0.0	22.3	59.7
Light Gas Oil	28.0	0.4	17.2	54.3

TABLE 4 Results of Example 4, Cellulose Acetate Butyrate Membrane and Middle Distillate

Sample	Weight %			
	Paraffins	Olefins	Naphthenes	Aromatics
Light Gas Oil	39.2	0.9	34.5	25.3
Liquid on High Pressure Side	38.9	1.0	36.3	23.8
Permeate	33.1	3.1	34.1	29.7
Liquidon High Pressure Side	38.4	2.1	34.3	25.1
Permeate	34.1	2.1	30.9	33.6

Figure 1 Reverse Osmosis Fractionation Schematic

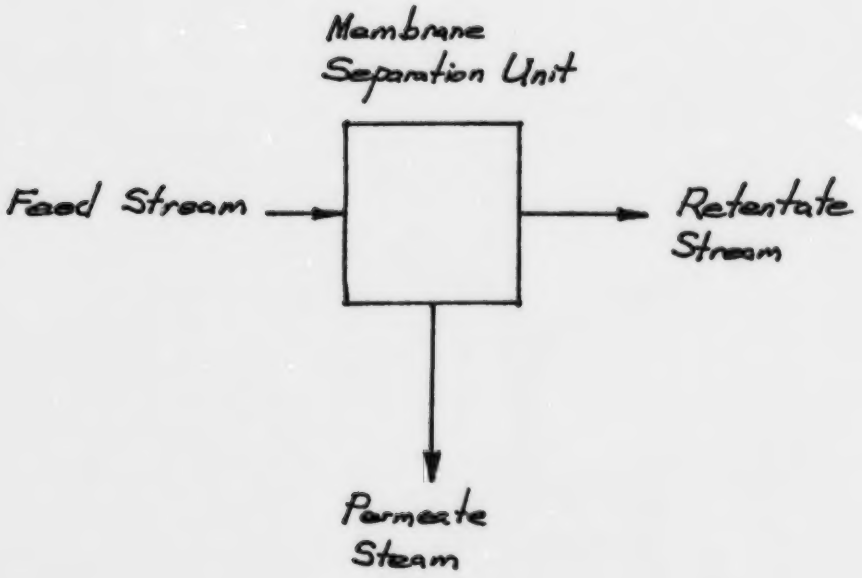

Figure 2 Static Reverse Osmosis Cell

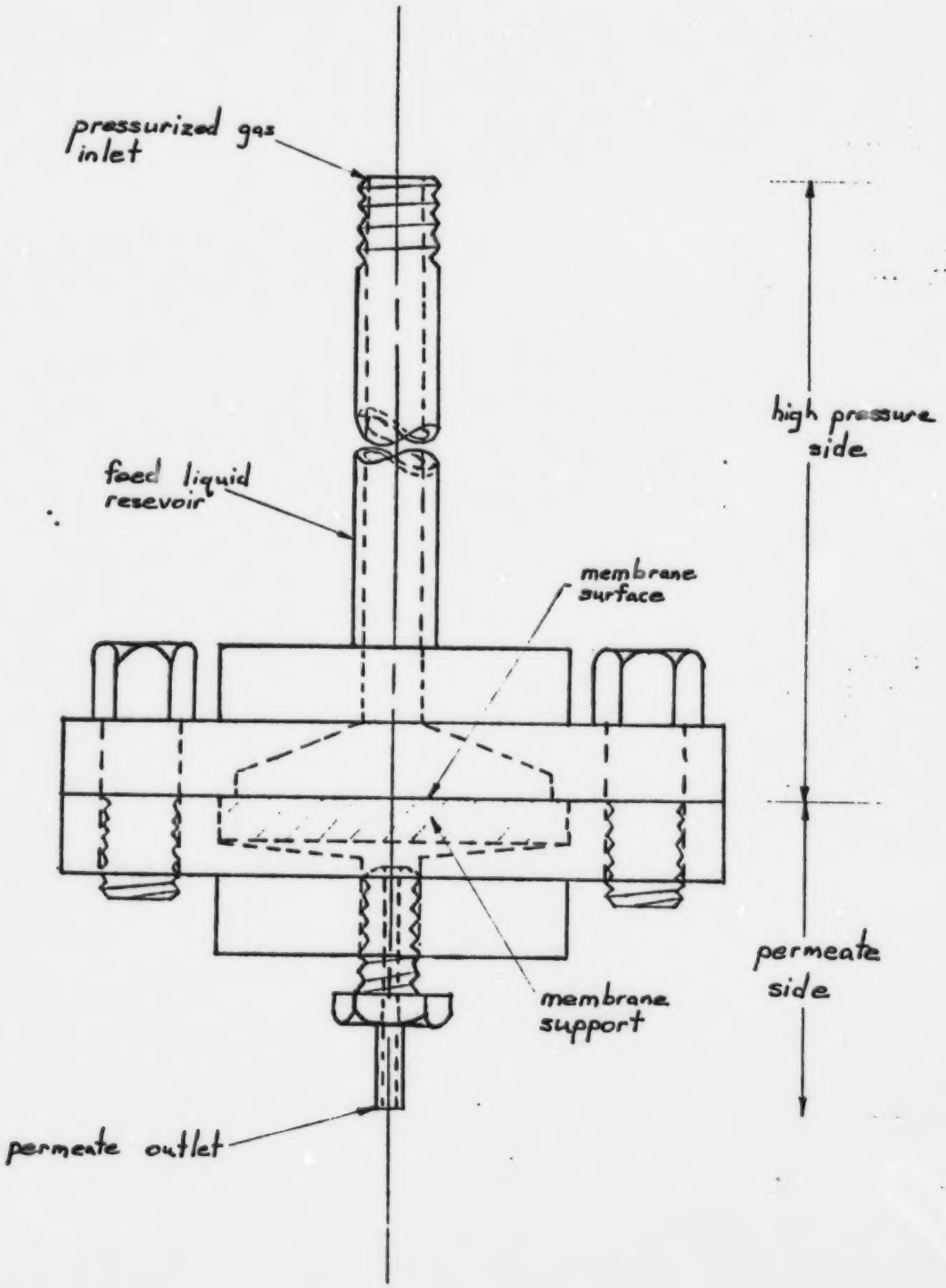

Figure 3 Continuous Membrane Separation Process Schematic (Single Stage)